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MEMBRANE MATERIALS FOR WASTEWATER RECLAMATION BY REVERSE OSMOSIS

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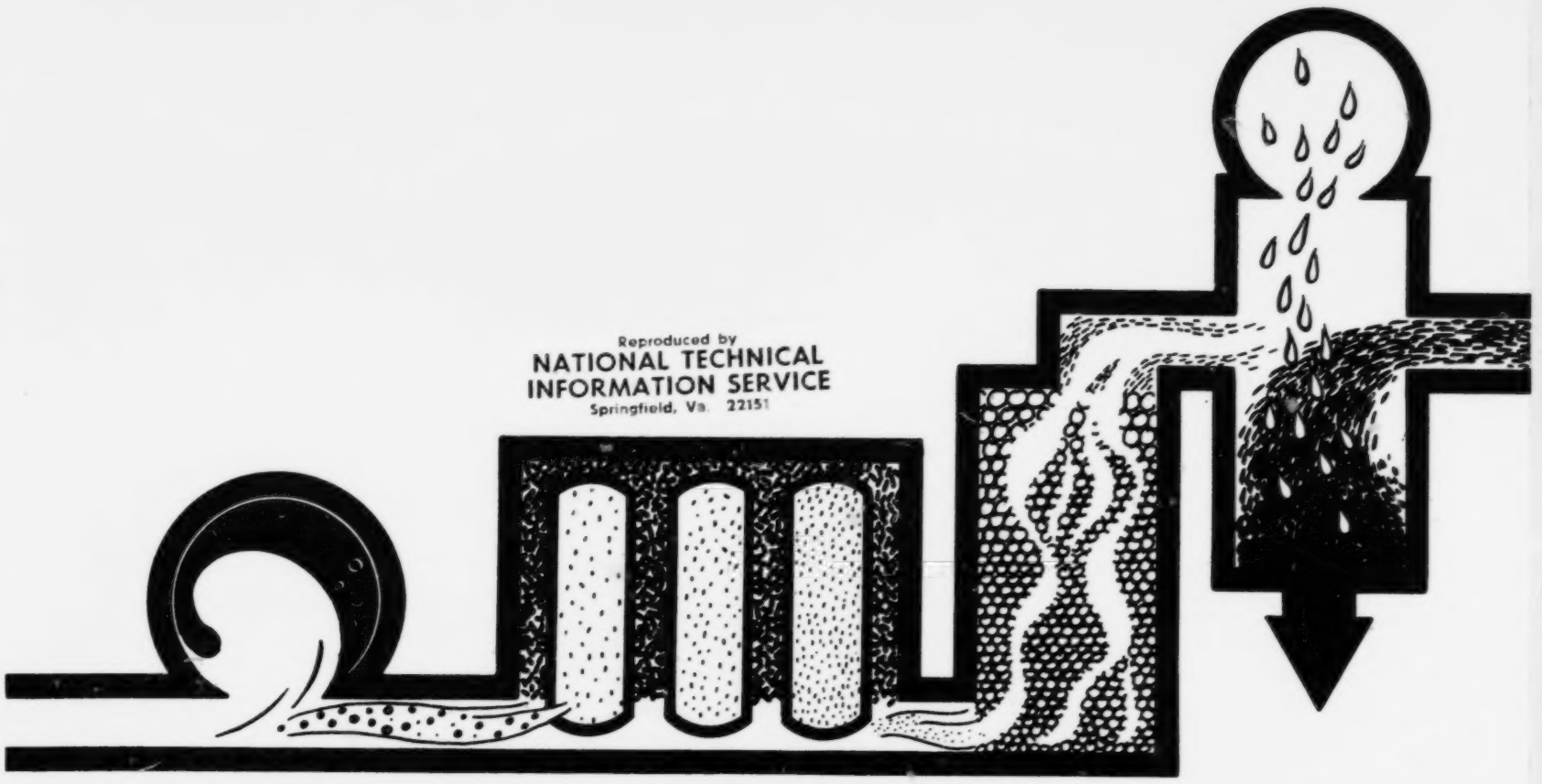

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The cellulose diacetate, polyurethane latices, and PVP membranes were not suitable for waste-water treatment. Although rejection of most solutes by PVP membranes was quite good for dense, homogeneous membranes, high-flux, asymmetric membranes had poor rejection characteristics. Very-high-flux membranes were prepared from polyacrylic acid cast onto cellulose nitrate, cellulose nitrate-cellulose acetate, and polysulfone porous supports. While NaCl rejection of over 80% was obtained at fluxes of less than 20 gal/ft^2-day at 600 psi, increased flux was obtained only at the expense of good rejection. The best combination of high flux and rejection was obtained with asymmetric cellulose 2.5-acetate membranes heat-treated in water at 55° to 70°C.

Abstractor	Institution

MEMBRANE MATERIALS FOR WASTE WATER RECLAMATION BY REVERSE OSMOSIS

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for the

FEDERAL WATER QUALITY ADMINISTRATION

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ABSTRACT

An experimental program was carried out to evaluate potential reverse osmosis membranes for the tertiary treatment of secondary sewage effluent. The evaluation program consisted of both direct osmosis and reverse osmosis tests on various membranes using both single solutes and secondary effluent. The types of membranes tested were polyurethane latices, cellulose diacetate, cellulose 2.5-acetate, polyvinylpyrrolidone (PVP)-polyisocyanate interpolymers, and polyelectrolytes.

The cellulose diacetate, polyurethane latices, and PVP membranes were not suitable for waste-water treatment. Although rejection of most solutes by PVP membranes was quite good for dense, homogeneous membranes, high-flux, asymmetric membranes had poor rejection characteristics. Very-high-flux membranes were prepared from polyacrylic acid cast onto cellulose nitrate, cellulose nitrate-cellulose acetate, and polysulfone porous supports. While NaCl rejection of over 80% was obtained at fluxes of less than 20 gal/ft^2-day at 600 psi, increased flux was obtained only at the expense of good rejection. The best combination of high flux and rejection was obtained with asymmetric cellulose 2.5-acetate membranes heat-treated in water at 55° to 70°C.

This report was submitted in fulfillment of Contract 14-12-452 between the Federal Water Quality Administration and Gulf General Atomic.

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SECTION 1

CONCLUSIONS AND RECOMMENDATIONS

The most apparent conclusion to be drawn from this program is that, of the membranes surveyed, asymmetric cellulose 2.5-acetate, heat-treated in water at 55° to 70°C, was the best overall membrane for waste-water reclamation with regard to both flux and rejection characteristics.

Polyacrylic acid (PAA) membranes were prepared with transport properties that varied over a wide range, but in the flux range of interest for large-scale applications, the rejection needs to be improved. In general, heating the membranes in air at 80° to 110°C reduced the water flow and increased salt rejection. The reproducibility among PAA membranes was poor, and severe flux decline was in evidence over the first two days of operation. Attempts to restore membrane properties in situ to increase the flux characteristics produced only transient effects; within a few hours the flux had begun to decrease again. Efforts to form a dynamic PAA membrane on the surface of a cast PAA membrane resulted in no beneficial effects.

PVP-polyisocyanate interpolymer membranes had good rejection properties when the mole ratio of isocyanate to PVP was 0.9 or higher. However, high-flux asymmetric membranes of this material generally had poor rejection ability, and the rejection was not improved by heating the membranes.

Neither the cellulose diacetate nor the polyurethane latex membranes studied in this program were suitable for treatment of secondary effluent. These membranes generally showed poor transport characteristics.

Of the new membrane materials studied, only PAA shows any promise for commercial use and may be worth additional investigation. The best of these membranes had flux and rejection properties that were comparable to those of asymmetric cellulose 2.5-acetate membranes. The lack of reproducibility among nominally identical membranes is a severe problem and presumably is

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related to the casting technique and/or support properties. It is believed that the preparation of larger sheets of membrane on a continuous basis would improve this situation.

SECTION 2

INTRODUCTION

With increasing emphasis being placed on the problem of environmental pollution, new and improved methods for waste-water purification are in great demand. Treatment methods are being sought not only to purify domestic and industrial wastes to maintain or improve quality of the receiving waters, but also to meet the need for multiple water reuse that is expected to become vital in some areas in the 1980s. Municipal waste treatment facilities currently in operation generally utilize primary and secondary treatment steps. Primary treatment usually consists of settling to remove suspended solids, while secondary treatment involves the biochemical degradation of organic compounds. The secondary effluent may then be chlorinated and is finally discharged. Generally, a 90% (1) biochemical oxygen demand (BOD) removal is effected from an initial value of about 150 mg/liter in the raw sewage (2). The effluent also contains a significant amount of dissolved inorganic salts (usually about 200 to 300 mg/liter higher than the local water supply). In order to make this water suitable for reuse, both the organic compounds and inorganic salts must be substantially reduced.

Several schemes for lowering the level of impurities present in sewage effluent are currently under investigation. One process being studied uses activated carbon to remove the organic material followed by electrodialysis to remove the dissolved salts. Reverse osmosis has been proposed as another possible technique for tertiary treatment. One significant advantage of this process might be that both the organic material and the inorganic material could be removed in a single step. Reverse osmosis is currently undergoing field evaluation both at Pomona, California, and Lebanon, Ohio, under FWQA sponsorship. In both of these evaluations, cellulose acetate-based membranes limited to cellulose 2.5-acetate membranes made by the Loeb-Sourirajan technique (3) are being used.

The purpose of the present laboratory study was to develop new membrane materials that would be suitable for use with secondary effluent to provide a product water with 95% of the organic matter removed as well as 70% to 80% of the dissolved electrolytes. This product might be suitable for use as potable water.

Several different membrane materials were evaluated for use in waste-water treatment in this study, i.e., polyelectrolytes, PVP-polyisocyanate interpolymers, cellulose diacetate, and latex materials. For successful application, membranes must be effectively very thin (generally less than 1 μ) to allow a high water flux. (The Loeb-Sourirajan asymmetric cellulose acetate membrane has this characteristic.) Thus, the problem of membrane development is two-fold: (1) finding a membrane material with good transport properties, and (2) preparing an effectively thin film. Several methods have been develop for preparing a membrane with these properties:

1. The technique of Loeb and Sourirajan (3) has received wide application for preparing asymmetric membranes of cellulose 2.5-acetate. In this procedure, the polymer is dissolved in a mixture of a very volatile good solvent (acetone) and a poor solvent of low volatility (magnesium perchlorate in water). The resulting solution is cast on a glass plate (or steel belt); evaporation occurs for a short time; and the membrane is immersed in water to remove the remaining solvent and cause solidification of the structure. The resulting membrane has a thin, dense skin on the air-dried surface, and the rest of the structure is a porous open network. All the resistance to flow appears to be in the thin skin.

2. A composite membrane is currently under development at Gulf General Atomic (4)(5). This method allows the deposition of a thin layer of cellulose acetate (typically about 1000 Å thick) on the surface of a finely porous support. Rejections of greater than 99.5% NaCl have been obtained with membranes of this type.

3. Membranes with good transport properties have also been prepared by employing a variation of the Oak Ridge National Laboratory (ORNL) technique of dynamic membrane formation (6), i.e., depositing a small amount of a salt-rejecting material into pores of a finely porous support.

In the present study, high-flux membranes with substantial rejection of both organic and inorganic materials were prepared from various polyelectrolytes, with PAA membranes receiving the most attention. The earlier work at ORNL with dynamic PAA membranes had suggested that membranes cast on a suitable porous support may have good transport properties. Subsequent work at Gulf General Atomic (5) indicated that cast PAA membranes had properties that were in some ways superior to the dynamically formed membranes. Extensive testing of PVP-polyisocyanate interpolymers was conducted using thick homogeneous films. This system was reported to have good hydrolytic stability and should therefore have a significantly increased lifetime compared with that of cellulose 2.5-acetate, especially in mildly basic solution such as secondary effluent. Riley and co-workers (7) had shown that a series of hydrophilic materials could be prepared from this system with a wide range of water and salt permeabilities. Cellulose diacetate membranes were prepared and tested, since earlier measurements by Lonsdale and co-workers (8) had shown that the water permeability was a factor of six higher than that of cellulose 2.5-acetate generally used in reverse osmosis systems. The study of latex-based membranes was initiated as a result of an observation made in this laboratory (9) that a membrane prepared from Wyandotte E-207A latex provided more than 100 gal/ft^2-day (gfd) and 30% rejection using 1% NaCl feed at 1500 psi.

Membrane testing was performed using direct osmosis, reverse osmosis, and a "desorption rate" technique (10). Desorption rate and direct osmosis tests were used with homogeneous membranes to evaluate potential membrane materials without having to prepare membranes with sufficient strength to withstand the operating pressure of reverse osmosis. In particular, the desorption rate technique was quite useful, because accurate values of solute

diffusivity and permeability could be obtained even if a membrane contained imperfections. Membranes that showed favorable properties in desorption rate and direct osmosis measurements were then tested in reverse osmosis using single solute feeds, and, in some cases, filtered secondary effluent.

SECTION 3

EXPERIMENTAL

MEMBRANE PREPARATION

CELLULOSE 2.5-ACETATE

Homogeneous cellulose 2.5-acetate membranes were prepared from Eastman E 398-10* cellulose acetate (15 wt-% in dioxane) by casting onto a glass plate with a doctor knife. The membrane was enclosed in a Plexiglas box to retard the rate of solvent removal, and the solvent was allowed to evaporate overnight. Asymmetric membranes were made of the same material by the method of Sourirajan and Govindan (11) from a mixture of cellulose acetate, acetone, water, and magnesium perchlorate. The membrane was cast on a glass plate at approximately 5°C and, after 3 to 4 min, was immersed into ice water for about 1 hr. The membrane properties were then altered by a heat treatment in water ranging from 55° to 80°C, depending on the flux and rejection desired.

POLYELECTROLYTES

Membranes were prepared from several polyelectrolytes and evaluated in reverse osmosis tests. These materials included:

1. American Cyanamid Company Cyanamer A-370 (modified sodium polyacrylate)

2. American Cyanamid Company Cyanamer P-26 (acrylamide copolymer)

---

*Mention of commercial products does not imply endorsement by the Federal Water Quality Administration.

3. Stein-Hall Polyhall-295 (high-molecular-weight (MW) anionic polyacrylamide)

4. Stein-Hall Polyhall-402 (high-MW nonionic polyacrylamide)

5. General Aniline and Film (polyvinyl methyl ether-maleic acid copolymer)

6. Rohm and Haas Acrysol A-1 and A-5 (PAA; 50,000 and 300,000 MW, respectively)

7. PAA, 10^6 MW (synthesized in this laboratory) (5)

The polyelectrolyte membranes were prepared on porous supports by both dipping and casting from several concentrations in water solutions, ranging from 0.04 to 25 wt-%. The dipping procedure consisted of preparing a dilute (2% or less) solution of the polyelectrolyte in water and immersing a porous support (see below) taped to a glass plate. The plate was withdrawn at a controlled rate, then allowed to drain and air-dry. In some cases, membranes were prepared by dipping several times, with air-drying between immersions.

Membranes were also cast from more concentrated (1% to 25%) polyelectrolyte solutions onto similar porous supports and air-dried before use. The solution was applied to the support by spreading with a glass rod. Thickness measurements of eight membranes cast from 4.8 wt-%, 10^6-MW PAA showed an average thickness of the PAA film ranging from 2.4 to 5.6 μ after air-drying and heat-treating at 110°C. These measurements were made using a Federal thickness gauge (Model P11). No attempt was made to determine to what extent the PAA penetrated the pores of the support. The uniformity of the membrane was not believed to be critical, since much of the polyelectrolyte film was washed off during testing in reverse osmosis. The effects on these membranes of heat-treating in air were also studied.

PVP-POLYISOCYANATE INTERPOLYMERS

Homogeneous PVP-polyisocyanate interpolymer membranes were prepared by casting from a 7 to 15 wt-% solution in chloroform. The PVP used in these studies was General Aniline and Film K-90. Two isocyanates were studied: polymethylene polyphenyl isocyanate, or PMPI (Upjohn Company PAPI); and methylenebis-(4-phenyl isocyanate), or MDI (Matheson Coleman and Bell).

Studies performed in this laboratory showed that the isocyanates polymerize or self-crosslink in the presence of water, forming an insoluble interpolymer network with the PVP. In the case of the trifunctional PMPI, a three-dimensional network is formed, whereas the difunctional MDI is restricted to the formation of a linear polymer lattice. In some cases, the PMPI was used as a stabilized material with the isocyanate groups blocked with ε-caprolactam (Upjohn Company Isonate 123 P). This material is destabilized at temperatures above about 150°C, and the isocyanate groups are made available to react with water vapor to form a three-dimensional structure.

Membranes were prepared from solutions containing isocyanate-to-PVP molar ratios in the range from 0.7 to 1.0. When blocked PMPI was used as the isocyanate, which was the case for all homogeneous films, the membranes, after drying in air, were heated slowly to 150°C and held at that temperature for 1 hr. The PVP-MDI membranes were cast under anhydrous conditions, and after the solvent evaporated, water vapor was admitted at a slow rate to cause reaction without rapid evolution of CO_2, which would result in the formation of bubbles in the membrane. Details of these procedures are given in (7).

Asymmetric membranes were prepared by adapting the procedures of Loeb and Sourirajan for cellulose 2.5-acetate membranes. Low-volatility solvents were sought which would remain in the film when the chloroform evaporated and which were relatively poor solvents themselves, so that after the chloroform was gone the polymer would precipitate as a fairly

porous open structure. Both short drying times and overnight drying were used in an attempt to vary the film properties.

The unblocked PMPI was added to a solution of PVP in chloroform so that the ratio of moles of PVP to equivalents of PMPI was 1:1. The weight ratio was 0.84 g PVP:1.0 g PMPI. The solid PVP and liquid PMPI were miscible in chloroform at room temperature. A 10 wt-% stock solution was prepared to which nonvolatile components could be added. The solution was kept anhydrous to prevent the reaction of the isocyanate with water. To this stock solution several miscible organic liquids were added, including tetrahydrofuran (THF), pyridine, THF-pyridine mixtures, triethyl phosphate, and amyl acetate. Solutions were prepared volumetrically. For example, a solution of 30% THF was prepared by adding 30 volumes of THF to 70 volumes of the stock solution.

Following the Loeb-Sourirajan technique, the membranes were cast in the room atmosphere at approximately 70°F and 50% relative humidity. After a drying period ranging from 5 min to 24 hr, they were immersed in water at room temperature. Simultaneously with the drying, the isocyanate reacted with water vapor in the atmosphere to form the interpolymer network. The resulting films were not uniform, but, in general, had a brownish air-dried surface and an opaque-white bottom surface. The opacity indicates the presence of light-scattering centers, suggesting the presence of porosity. Further evidence of porosity was obtained from dye tests. The bottom surface absorbed a water-soluble dye painted on it; the air-dried surface rejected the dye.

CELLULOSE DIACETATE

Homogeneous cellulose diacetate membranes were prepared from Eastman E 360 cellulose diacetate dissolved in reagent-grade pyridine. The membranes were cast onto a glass plate and were allowed to evaporate to dryness in a closed box.

LATEX

Several different latex materials were evaluated:

1. Wyandotte Chemical Company E-207A (nonionic polyurethane)

2. Wyandotte Chemical Company X-1017 (anionic polyurethane) (very small particle size)

3. GAF Polectron 450 (PVP-styrene copolymer)

4. General Latex RA-150-7

Membranes were prepared from these latices by several different techniques. One technique was to dilute them with water to the desired solids content and then cast directly onto a cellulose nitrate-cellulose acetate porous support. The water was evaporated to dryness, and permeability properties were then measured in reverse osmosis tests. The effect of heat-treating in air at several temperatures for various times was also examined. In a second technique, the latex was formed into a solution by the addition of ethanol, and this clear solution was cast onto the support. The solvent was evaporated to dryness and testing proceeded as before. In some cases, metal salts such as magnesium and calcium chlorides were added to the latex in an effort to reduce the effect of the stabilizing surfactant and permit a more continuous film to form.

POROUS SUPPORTS

Three types of support materials were prepared for use with polyelectrolyte membranes: cellulose nitrate-cellulose acetate (CN/CA), polysulfone, and cellulose nitrate (CN).

CN/CA

The procedure for preparing this support has been described previously (4). The casting solution consists of CN (du Pont DHA 35 E) and CA (Eastman 383-40) in the weight ratio of 86:14 dissolved in a solvent system consisting of acetone, ethanol, n-butanol, water, Rohm and Haas Triton X-100, and glycerin. The support is cast onto a glass plate and dried in air at approximately 100% relative humidity. The resulting membrane is finely porous with a bulk porosity of about 60%. The CN/CA porous supports showed a water flux of approximately 700 to 3500 gfd when tested with distilled water in a low-pressure system at 40 psi.

Polysulfone

Polysulfone porous supports were prepared by casting a film of polysulfone (Union Carbide 3500) in dimethyl formamide (approximately 6 to 20 wt-%) onto a glass plate and rapidly immersing the film in water at approximately 5°C. Although at 40 psi the water flux of the wet membrane is comparable to that of CN/CA, the air-dried support shows a considerable reduction in flux, and in some cases no flux at all. This behavior is attributed to the hydrophobic character of polysulfone (i.e., the lack of ability to readily absorb water) and not to a reduction in porosity upon drying. Such flux reduction is generally not a problem in reverse osmosis measurements because of the higher applied pressure. (Polyelectrolyte membranes with initial water fluxes greater than 300 gfd at 600 psi have been prepared using this support material.)

CN

The preparation of finely porous CN membranes has been described by Baddour, Vieth, and Douglas (12). The method consisted of dissolving CN in a solvent to which certain soluble inorganic salts were added. After casting the membrane, the solvent was allowed to evaporate and the salt was completely

removed by leaching in water to produce a porous membrane. Porous membranes prepared in this manner using $CaCl_2$ or $ZnCl_2$ were found to be unsatisfactory as a support for polyelectrolyte membranes because of excessive shrinkage upon drying.

A CN support with minimal shrinkage upon drying was prepared by incorporating anhydrous $CrCl_3$ with CN in acetone. A coordination complex trichlorotri-acetone chromium (III), $[Cr(C_3H_6O)_3Cl_3]$, was prepared according to the procedure of Taylor and Milstead (13) by extracting $CrCl_3$ and a trace of a reducing agent (zinc powder) in a Soxhlet extractor with acetone. At the conclusion of the extraction, CN was dissolved in the $CrCl_3$-acetone solution to form a casting solution of 6 wt-% CN and 16 wt-% $CrCl_3$. The membrane was cast on a glass plate and sealed in a closed box to allow slow evaporation of the acetone. The film was then exposed to high-humidity air until the conversion of the $CrCl_3$-acetone complex to $CrCl_3 \cdot 6H_2O$ was complete. The formation of the hydrated $CrCl_3$ in the film was accompanied by a color change from violet to a bright green. The $CrCl_3 \cdot 6H_2O$ was washed from the membrane with water, yielding a porous CN membrane with properties similar to those of the CN/CA support. Dry CN support material was prepared which had water fluxes ranging from 100 to 2700 gfd when tested at 40 psi.

METHODS OF MEASUREMENT

The permeabilities of the dense homogeneous membranes to water and solutes were determined by both direct osmosis and reverse osmosis, and in some cases the distribution coefficient and diffusivity of solutes were independently measured in "desorption rate" experiments. In addition, diffusivity and distribution coefficients for some membranes were obtained from time-lag measurements in direct osmosis.

DIRECT OSMOSIS

For the direct osmosis tests, a two-compartment cell, which had a membrane area of 262 cm^2, was used; the volume on each side of the cell was 2.7 liters. Internal stirring was provided by a glass paddle connected through

a rotary seal to an external motor. The cell was immersed in a 25°C constant temperature bath. For a given run, the homogeneous membrane was first equilibrated with distilled water on both sides. The experiment was started by introducing a known amount of concentrated solution of the solute (chosen to give a desired concentration in the cell to provide a high osmotic pressure difference and therefore a high water flux) at the top of one side of the cell. Mixing was complete within about 15 sec. When the solute was an electrolyte, a conductivity probe was placed in the distilled water on the other side of the cell. The conductivity of the solution was monitored with a Beckman Instruments conductivity cell (Models CEL-VY001 and -002, cell constants 0.01 and 0.02 cm^{-1}, respectively) and a Solu Meter (Model RA5) connected to a 10-mV recorder. The sensitivity of the measurements was 0.23 ppm NaCl/mV using a conductivity cell of 0.01 cm^{-1} cell constant. A diagram of the apparatus with the conductivity probe in place is shown in Fig. 1. The rate of solute transport was calculated from the known calibration of the conductivity probe.

For the nonelectrolytes, continuous analyses were performed with a Waters Associates Model R-4 recording differential refractometer. The dilute solution was continuously pumped through small-diameter polyethylene tubing to the refractometer and back into the cell by means of a Cole-Parmer Masterflex peristaltic pump (Model 7020V-13). Distilled water flowed by gravity through the reference side of the differential refractometer. The electrical output of the instrument was connected to a 50-mV recorder. At a sample flow of 11.0 cc/min and a reference distilled water flow of 0.8 cc/min, most solutes gave a reading of 0.5 to 2 mV for each milligram of solute per liter. The calibration for each solute was determined by a five-point standardization curve in the concentration range of interest; in this range, the refractive index is a linear function of concentration. The concentration of solute employed was 10%, and the experiment was terminated before the dilute side concentration was above about 100 mg/liter, so that the concentration gradient was essentially constant for each run. The water permeability was measured from the osmotic flow of water through the membrane by carefully filling the cell to exclude air bubbles at the start and measuring the osmotic water overflow from the concentrated side of the cell as a function of time.

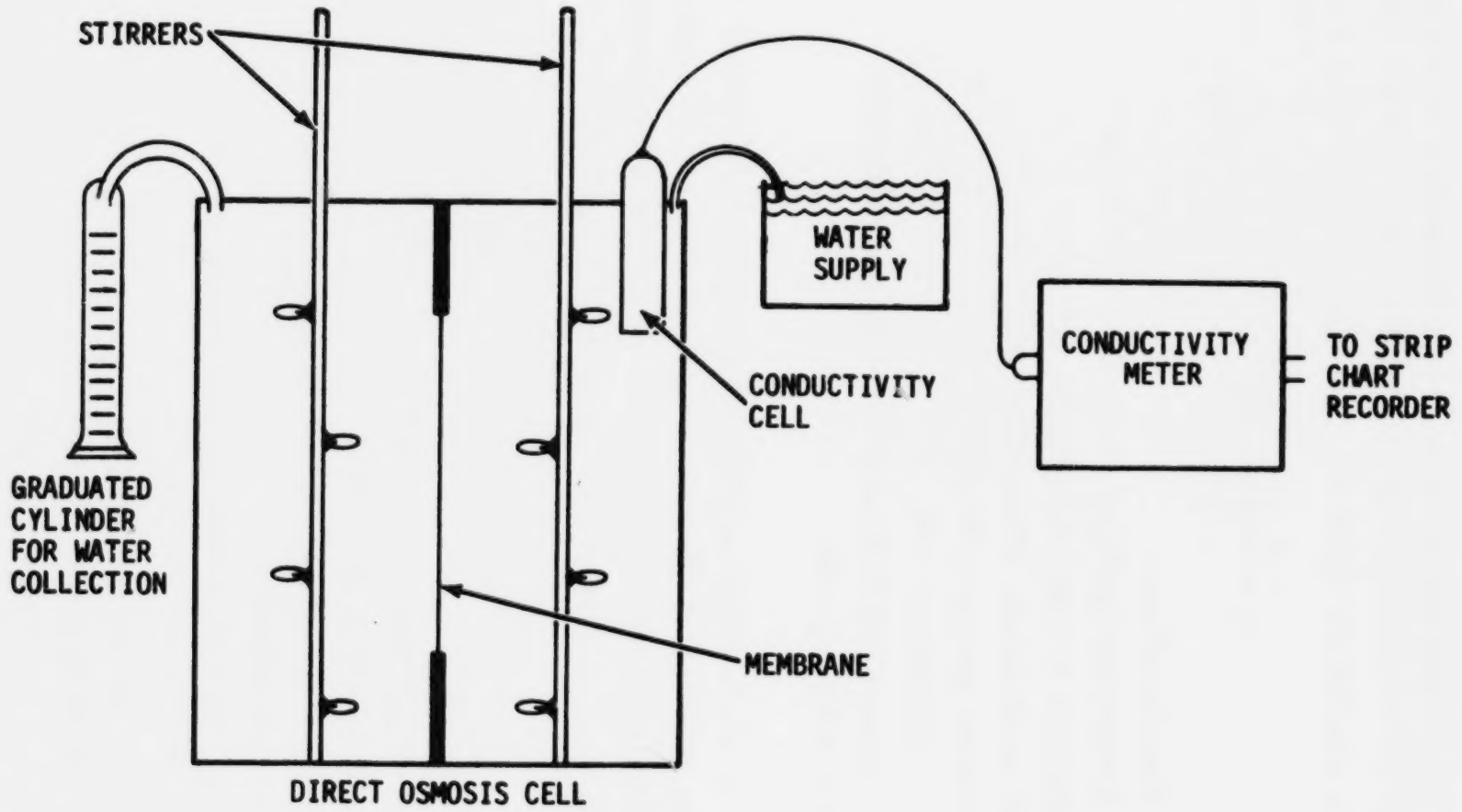

Fig. 1. Direct osmosis equipment for monitoring electrolyte and water transport

The permeability of the membrane to water (D_1c_1, the product of diffusivity and concentration) was calculated from the measured rate of water flow in the direct osmosis experiments using the following equation (14):

$$J_1 = \frac{D_1 c_1 \bar{v}_1}{RT} \left(\frac{-\Delta\pi}{\Delta x}\right) \quad , \tag{1}$$

where J_1 = water flow (g/cm^2-sec)
D_1 = water diffusivity (cm^2/sec)
c_1 = concentration of water in membrane (g/cc)
$\bar{v}_1$ = partial molal volume of water (cc/mole)
R = gas constant [cc-atm/(°K)(mole)]
T = absolute temperature (°K)
$\Delta\pi$ = osmotic pressure difference across the membrane (atm)
Δx = membrane thickness (cm)

The permeability of the membrane to the solute, D_2K, was calculated from the change in concentration of the dilute solution with time. A typical concentration-versus-time curve is shown in Fig. 2. The straight-line portion is described by an integrated form on Fick's law (15):

$$J_2 = -D_2K \frac{\Delta\rho_2}{\Delta x} \quad , \tag{2}$$

where J_2 = rate of solute transport (g/cm^2-sec)
D_2 = solute diffusivity (cm^2/sec)
K = solute distribution coefficient (g solute/cc membrane)/(g solute/cc solution)
$\Delta\rho_2$ = difference in solute concentration across the membrane

Therefore, D_2K can be calculated from the flux and the concentration difference across the membrane.

Extrapolation of the linear portion of the curve at long times to the base line gives the "time lag" for the membrane and allows one to calculate the solute diffusivity. The time lag, τ, is related to the diffusivity by the equation (16)

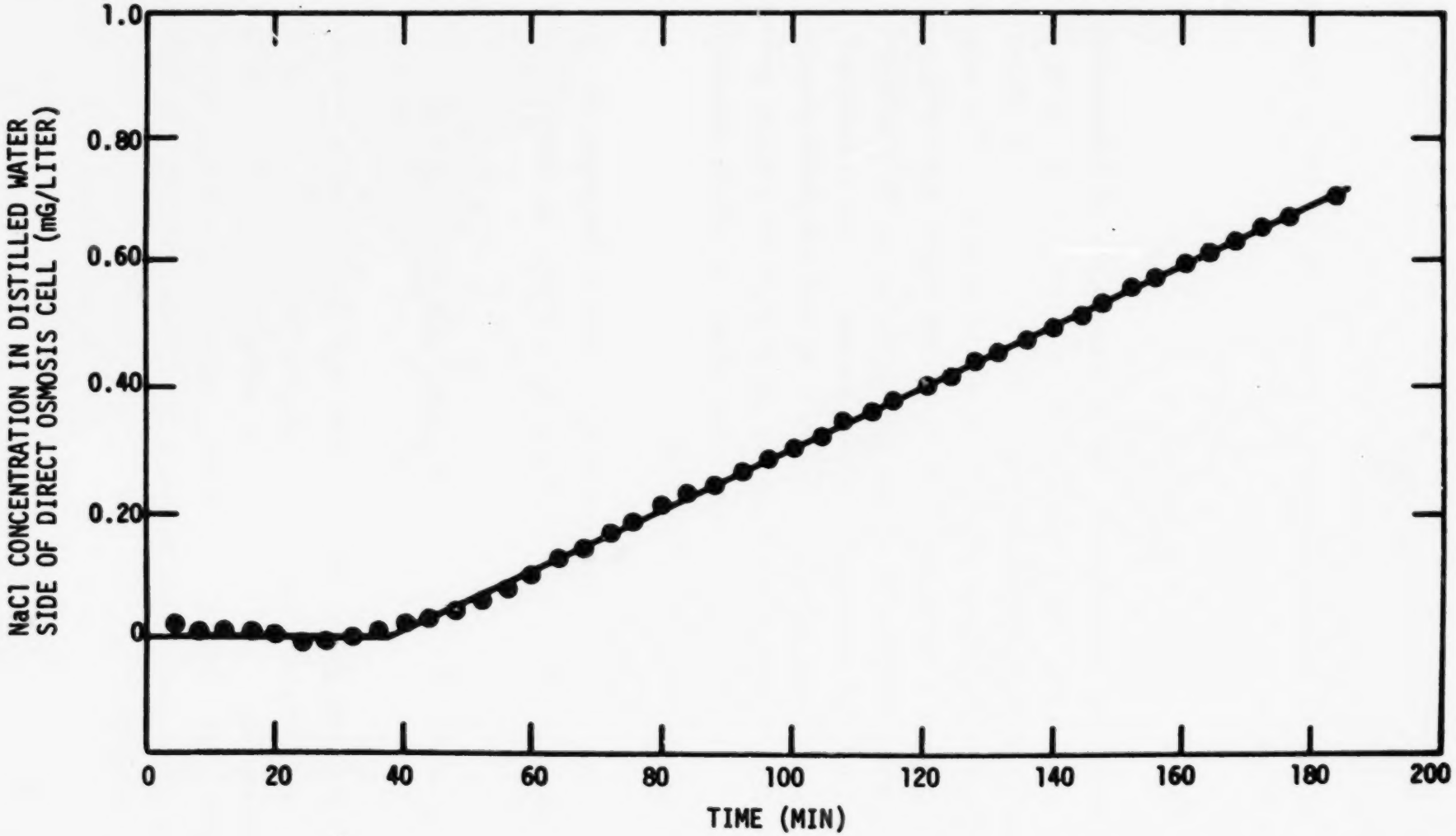

Fig. 2. Time lag experiment with NaCl (5% NaCl solution; membrane thickness, 70 μm) from (6)

$$\tau = \frac{(\Delta x)^2}{6D_2} \quad . \tag{3}$$

Then, the ratio of the permeability to the diffusivity is the solute distribution coefficient.

DESORPTION RATE

For the desorption rate experiments, 7/8-in.-diam disks of homogeneous membrane were equilibrated in a concentrated solution of the solute of interest. The disks were quickly rinsed in distilled water to remove any adhering droplets of concentrated solution and blotted dry. The membranes were then immersed in a known amount of distilled water, and, during desorption of solute, the increase in solute concentration in the distilled water was measured using the conductivity probe assembly or the refractometer described for the direct osmosis procedure. Details of these procedures are given in (10). The rate at which the desorption takes place is used to calculate the diffusivity, and the total amount of solute removal provides a measure of the distribution coefficient.

For diffusion into or out of a semi-infinite slab of thickness Δx, the relative concentration of the solute in the slab at time t is given by (15)

$$\frac{c_f - c_t}{c_f - c_o} = \frac{8}{\pi^2} \sum_{\nu=0}^{\infty} \frac{1}{(2\nu + 1)^2} \exp\left[-(2\nu + 1)^2 \frac{\pi^2 D_2 t}{\Delta x^2}\right] , \tag{4}$$

where c_f is the final concentration in the slab (i.e., the concentration at $t \to \infty$), c_o is the initial concentration, c_t is the concentration at time t, and D_2 is the diffusion coefficient. The higher-order terms of the series decrease rapidly, and at $t = 0.1\ \Delta x^2/\pi^2 D_2$, the second term is less than 5% of the first; for times longer than this, only the first term is important and Eq. 4 reduces to

$$\frac{c_f - c_t}{c_f - c_o} = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 D_2 t}{\Delta x^2}\right) . \tag{5}$$

Thus, a plot of ln $[(c_f - c_t)/(c_f - c_o)]$ versus time is a straight line [for $(c_f - c_t)/(c_f - c_o) < 0.7$] with a slope of $-\pi^2 D_2/\Delta x^2$, from which D_2 can be obtained, and an intercept of $8/\pi^2 = 0.81$.

REVERSE OSMOSIS

The reverse osmosis experiments were performed in a flow system (Fig. 3) that consisted essentially of a solution reservoir (or sump) maintained at atmospheric pressure, a high-pressure pump, an accumulator, a back-pressure regulator, and two parallel sets of three reverse osmosis cells, as well as gauges and other regulators. The volume of solution in the system was typically 54 liters. The flow system components on the high-pressure side were all fabricated from Monel, Type 316 stainless steel, or similar corrosion-resisting materials. The solution reservoir and interconnecting tubing on the low-pressure side were constructed of plastic. A 5-μ cartridge filter was installed between the reservoir and the pump. High-feed-solution flow was achieved with a Manton-Gaulin positive displacement triplex pump (Model MP-3) which has a rated capacity of 2 gpm. This pump permitted the high-pressure solution to be circulated at a high linear velocity (greater than 150 cm/sec) over the surface of the membrane, where boundary layer phenomena are known to be unimportant at the water fluxes observed in this work (17). Pressure fluctuations were damped to less than ±5 psi with the accumulator, and pressure drift during the measurements was essentially nil. Temperature was controlled at 25° ± 1°C.

The test cell contained a rectangular membrane approximately 1 in. by 3 in. (20-cm^2 area). The detailed design of the cell is described in (18). Testing was carried out at 1500 psi with the PVP membranes, at 800 psi with the latex membranes, and at 600 psi with the polyelectrolyte membranes. Water flow rates through the membrane were measured by collecting the output of a cell in a graduated cylinder for a known period of time. Solute concentrations in feed and product water were measured from conductivity for electrolytes and by use of a Beckman Instruments Carbonaceous Analyzer for non-electrolytes and secondary effluent.

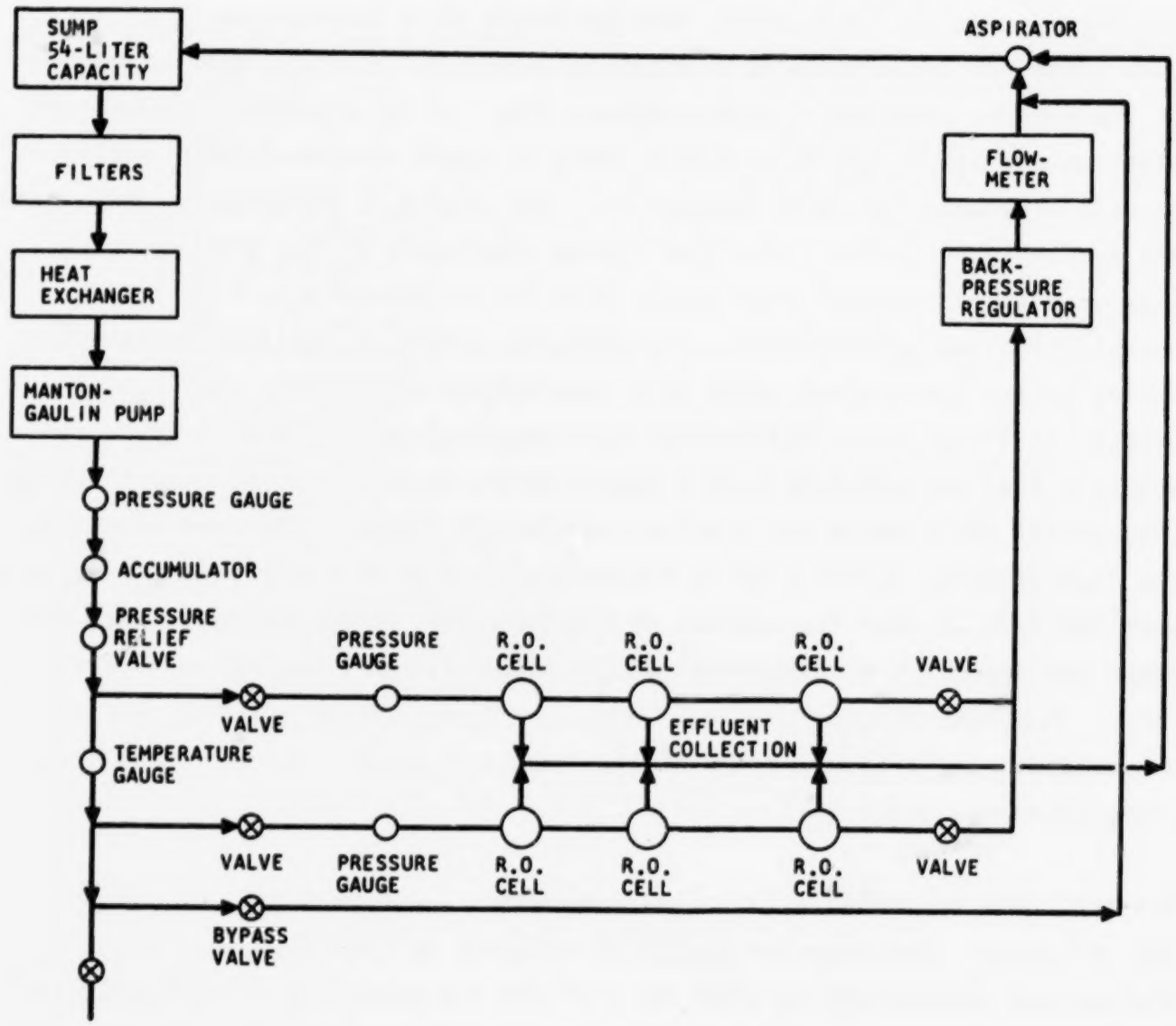

Fig. 3. Flow diagram of reverse osmosis system

In order to facilitate comparison of the reverse osmosis results and the direct osmosis measurements for the homogeneous films, the permeability of the membrane to water was calculated from the reverse osmosis results by the equation

$$J_1 = \frac{D_1 c_1 \overline{v}_1}{RT}\left(\frac{\Delta p - \Delta\pi}{\Delta x}\right) , \qquad (6)$$

where Δp is the applied hydraulic pressure and the other items are as previously defined. The direct osmosis and the reverse osmosis results for solute flux are directly comparable as long as transport is by a solution-diffusion mechanism only (14). In most cases permeability to solute can be calculated from Eq. 2. When solute rejection is poor, however, a slight revision is required. For that case, Lonsdale, Merten, and Tagami (19) have shown that the solute flux in reverse osmosis is given by

$$J_2 = \frac{-D_2 K \Delta\rho_2}{\Delta x} - \frac{D_2 K \rho_2' \overline{v}_2 \Delta p}{RT\Delta x} , \qquad (7)$$

where the prime refers to upstream concentration. The first term represents the contribution of the concentration difference to the flux, and the second term represents the contribution due to the pressure difference. The latter occurs as a result of the changing thermodynamic activity of the solute with pressure. Equation 7 can be written as

$$J_2 = \frac{-D_2 K \rho_2'}{\Delta x}\left[\frac{\Delta\rho_2}{\rho_2'} + \frac{\overline{v}_2 \Delta p}{RT}\right] . \qquad (8)$$

For sodium chloride, $\overline{v}_2$ is approximately 18 cc/mole (20), and the right-hand term within the brackets at 100-atm operating pressure is 0.073. For a highly rejecting membrane, $\Delta\rho_2/\rho_2' \simeq 1$, and the right-hand term in the brackets can be neglected, leaving a simplified form of Fick's law. If the rejection is not very good, Eq. 8 must be used to calculate solute permeability; otherwise, an apparent pressure dependence of the permeability will be observed.

The rejection of a solute is calculated by the equation

$$R = \frac{\rho_2' - \rho_2''}{\rho_2'} \quad , \tag{9}$$

where the double prime indicates the product water. The product water concentration is given by

$$\rho_2'' = \frac{J_2}{J_1 + J_2} \approx \frac{J_2}{J_1} \quad , \tag{10}$$

where the approximation holds because in the cases of interest here, $J_1 >> J_2$. Substituting into Eq. 9 yields

$$R = 1 - \frac{J_2}{\rho_2' J_1} \quad . \tag{11}$$

Substituting the equations for J_1 and J_2 (Eqs. 6 and 8) results in the following equation:

$$R = 1 - \frac{D_2 K R T \Delta\rho_2}{D_1 c_1 \bar{v}_1 (\Delta p - \Delta\pi)\rho_2'} - \frac{D_2 K \bar{v}_2 \Delta p}{D_1 c_1 \bar{v}_1 (\Delta p - \Delta\pi)} \quad . \tag{12}$$

Because $\Delta\rho_2/\rho_2'$ is the rejection, this equation can be simplified to give

$$R = \frac{D_1 c_1 \bar{v}_1 (\Delta p - \Delta\pi) - D_2 K \bar{v}_2 \Delta p}{D_1 c_1 \bar{v}_1 (\Delta p - \Delta\pi) + D_2 K R T} \quad . \tag{13}$$

When rejection is high, this equation reduces to

$$R = \frac{D_1 c_1 \bar{v}_1 (\Delta p - \Delta\pi)}{D_1 c_1 \bar{v}_1 (\Delta p - \Delta\pi) + D_2 K R T} \quad . \tag{14}$$

The required permeabilities were measured in direct osmosis experiments, and the choice of an operating pressure permitted direct calculation of the predicted rejection. This value was then compared with the value measured in reverse osmosis. Values for partial molal volumes and osmotic pressures were obtained from the literature (21).

SECTION 4

RESULTS AND DISCUSSION

POLYELECTROLYTE MEMBRANES

Polyelectrolyte membranes were evaluated only in reverse osmosis tests. Direct osmosis and desorption rate experiments could not be conducted since it was not possible to prepare a free-standing membrane. All membranes were tested at 600 psi and 25° ± 1°C with 0.1% NaCl. Unless otherwise indicated, all data were obtained after 16 to 20 hr, i.e., overnight tests, when the initial rapid changes in membrane properties had subsided. Asymmetric cellulose 2.5-acetate membranes were tested under the same conditions to serve as control membranes during polyelectrolyte membrane evaluation.

Several factors were investigated during this program: (1) type of polyelectrolyte, (2) molecular weight, (3) porous support, (4) method of membrane preparation, and (5) postcasting treatment conditions. Membranes were prepared on three types of porous support: CN/CA, polysulfone, and CN. The surface pore size of the CN and CN/CA supports was estimated from electron microscopy to be in the range 1000 to 3000 Å. No pores were detectable in the air-dried polysulfone.

An extensive investigation of membranes prepared from PAA was conducted, since this material seemed to offer considerable promise for preparing high-flux membranes suitable for waste-water purification.

Polyacrylic acid membranes were prepared from three different molecular-weight materials: 50,000, 300,000, and approximately 10^6 MW. Membranes prepared from 50,000-MW PAA gave essentially no NaCl rejection, apparently because this material was not retained by the porous support, and its use was therefore discontinued. Table 1 shows flux and rejection properties of membranes prepared from 300,000-MW PAA, both by casting and dipping. The effect of support type and low-pressure water flux as well as postcasting treatment is shown.

TABLE 1
TRANSPORT PROPERTIES OF PAA MEMBRANES
PREPARED FROM 300,000-MW PAA

Support Properties		Membrane Preparation			NaCl Rejection (%)	Water Flux (gfd)
Type	Water Flux at 40 psi (gfd)	Method	Wt % PAA	Heat Treatment		
CN/CA	3500	Cast	25	None	50	36
					50	37
					46	46
					46	43
		Dip	2.0		28	55
					25	60
				80°C, 1 hr	29	56
					32	60
				110°C, 1 hr	45	28
	800	Cast	25	None	57	23
					57	21
		Dip	2.0		88	16
					78	16
					88	17
					85	23
				80°C, 1 hr	75	22
					87	17
				110°C, 1 hr	87	4.6
					88	3.5
				115°C, 1 hr	97	0.8
					86	2.2
					96	1.1

TABLE 1 (Continued)

Support Properties		Membrane Preparation			NaCl Rejection (%)	Water Flux (gfd)
Type	Water Flux at 40 psi (gfd)	Method	Wt % PAA	Heat Treatment		
Polysulfone	(a)	Cast	25	None	54	59
				↓	54	56
				80°C, 1 hr	54	39
				↓	58	40
				110°C, 1 hr	67	38
				↓	61	38
		Dip	2.0	None	57	42
				↓	19	36
				80°C, 1 hr	58	38
				↓	68	33
				110°C, 1 hr	48	50
				↓	46	46
CN	400	Cast	25	None	32	96
↓	↓	↓	↓	↓	32	100
					32	101

(a) No flow through air-dried support at 40 psi.

These data indicate that both flux and rejection are dependent on the porosity of the CN/CA porous support, as characterized by the water flux of the support measured at 40 psi. A higher flux is accompanied by a lower rejection for the support with a 3500-gfd water flux. Heating the air-dried membranes at 80°C for 1 hr had little effect on either flux or rejection, but heating at 110° to 115°C caused significant decrease in the flux and an increase in the rejection. This difference in behavior is attributed to a reaction between the acidic groups of the PAA and the hydroxyl groups of the CN/CA. It is noted that heat treatment of the PAA-polysulfone membranes had essentially no effect on their transport properties. The PAA-polysulfone membranes show somewhat higher flux and rejection than do the PAA-CN/CA membranes. The three PAA-CN membranes tested show fluxes a factor of two to three greater than the other membranes but lower rejection.

These data are shown in Fig. 4 as a plot of flux versus rejection. For comparison, data for a set of asymmetric cellulose 2.5-acetate membranes heat-treated in water at various temperatures (Table 2) are also plotted. It can readily be seen that the cellulose 2.5-acetate membranes are superior to the PAA membranes; i.e., they show higher flux at the same rejection.

Tables 3, 4, and 5 show the transport properties of membranes prepared from 10^6-MW PAA on CN/CA, polysulfone, and CN, respectively. The overall properties of the PAA-CN/CA membranes (Table 3) are inferior to those of the other membranes, and the fluxes are generally lower than for the 300,000-MW PAA membranes. It is noted that reproducibility in the membrane properties is poor, particularly among the cast membranes where the flux ranges from 1.4 to 65 gfd for nominally the same membranes. No apparent benefit was observed by initially casting with a 1.2% 10^6-MW solution and then dipping the air-dried membrane in a 2.0% solution of lower-MW PAA.

Table 4 shows the properties of 10^6-MW PAA prepared on high-flux polysulfone supports. The support is characterized by using the low-pressure flux of the wet material, since upon drying the support loses much of its flow at 40 psi and does not rewet easily because of its hydrophobic nature. The problem of reproducibility of these membranes is not as severe as noted for the PAA-CN/CA

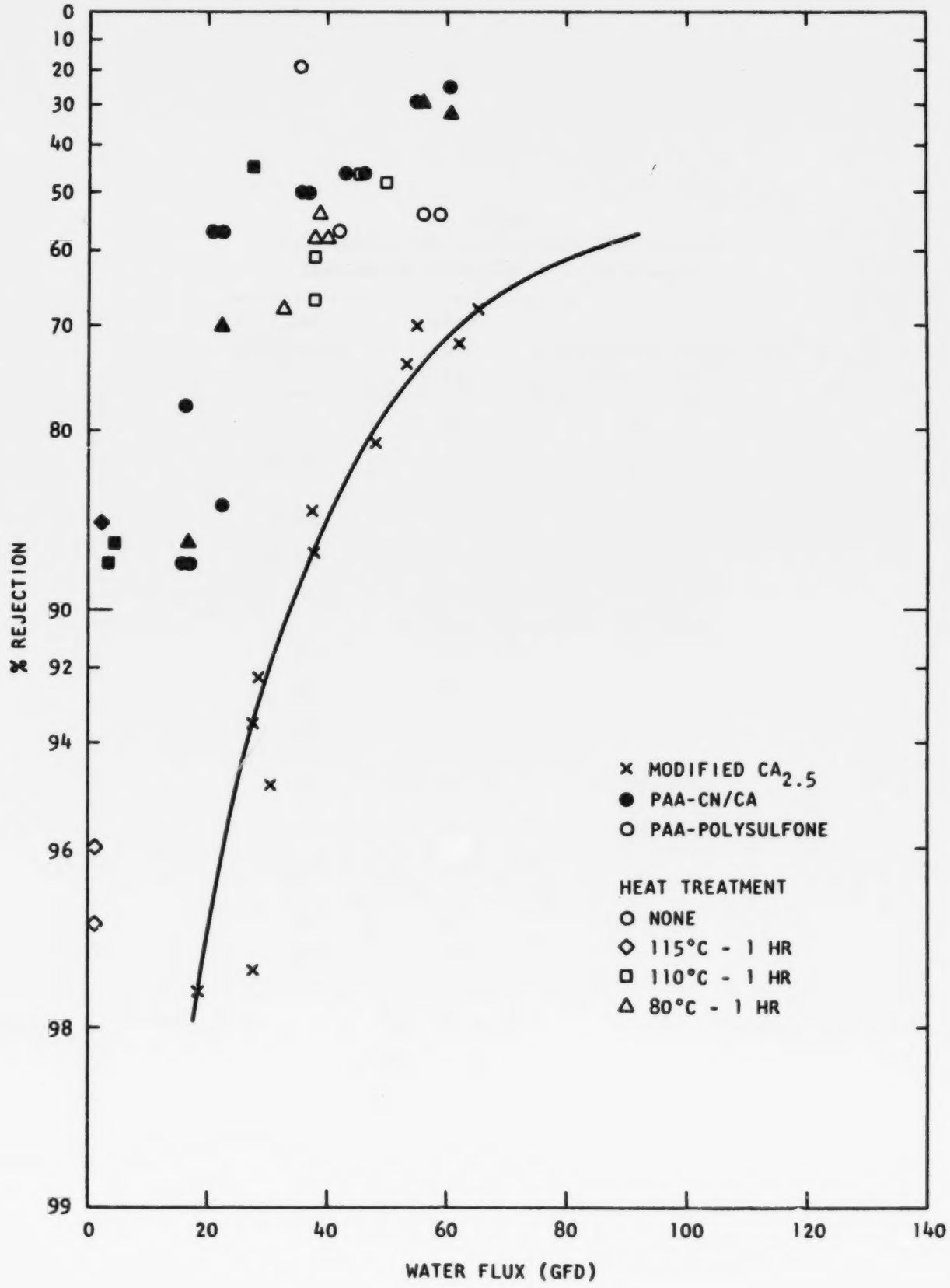

Fig. 4. Flux-rejection data for 300,000-MW PAA membranes on CN/CA and polysulfone porous supports

TABLE 2
TRANSPORT PROPERTIES OF ASYMMETRIC CELLULOSE 2.5-ACETATE MEMBRANES

Heat Treatment (°C, 5 min)	Water Flux (gfd)	NaCl Rejection (%)
80	18	97.7
80	27	97.5
75	30	94.9
75	28	93.5
75	28	92.3
70	41	89
70	38	88
70	37	86
60	48	81
55	55	70
55	53	76
55	62	72
55	65	68

TABLE 3
TRANSPORT PROPERTIES OF PAA MEMBRANES PREPARED FROM 10^6-MW PAA ON CN/CA POROUS SUPPORT

Water Flux of Support at 40 psi (gfd)	Membrane Preparation			NaCl Rejection (%)	Water Flux (gfd)
	Method	Wt % PAA	Heat Treatment		
3500	Cast	1.2	None	44	58
				39	65
				84	1.4
				84	1.6
				90	3.4
				94	3.3
				36	49
				33	53
	Cast (10^6) + dip (50,000)	1.2 + 2.0		29	64
				29	73
	Cast (10^6) + dip (300,000)			48	59
				43	62
	Dip	0.2		66	22
				64	19
				68	19
1400				70	11
				79	7.4
				81	3.1
700				82	10
				81	10

TABLE 4
TRANSPORT PROPERTIES OF PAA MEMBRANES PREPARED FROM 10^6-MW PAA ON POLYSULFONE POROUS SUPPORT

Water Flux of Wet Support at 40 psi (gfd)	Membrane Preparation			NaCl Rejection (%)	Water Flux (gfd)
	Method	Wt % PAA	Heat Treatment		
~2900	Dip	0.5	None	34	11
				38	23
				38	40
~2000		0.2		46	94
				34	76
				40	80
				31	120
				33	115
				38	74
				35	91
			80°C, 1 hr	39	58
				44	103
			110°C, 1 hr	60	53
				39	153
				43	135
				44	54
				42	64
	Cast		None	38	92
				39	85
			110°C, 1 hr	35	74
				58	94
		0.2 in 1:1 EtOH	None	30	100
			110°C, 1 hr	35	97
~10,000		4.8	None	50	18
				52	20
				53	22
~4000				55	11
				55	12
				56	8.5

TABLE 4 (Continued)

Water Flux of Wet Support at 40 psi (gfd)	Membrane Preparation			NaCl Rejection (%)	Water Flux (gfd)
	Method	Wt % PAA	Heat Treatment		
~2900	Cast	4.8	None	42	97
				60	69
				51	74
				40	113
			110°, 1 hr	70	19
				70	33
				59	90
				56	99
				42	131
				45	134
				60	87
				56	73
				42	133
				52	104
			115°C, 1/2 hr	60	112
				51	150
				53	136
				47	150
				42	173
				58	110
			120°C, 1/2 hr	--	0
~7000		1.3	None	18	173
			110°, 1 hr	0	440
		1.3 (2 coats)	None	0	457
		1.3 + 2.1		35	131
				56	62
				43	82
				38	98
				60	53
~4000		2.6		28	26
				28	24
		1.3.		58	14

TABLE 5
TRANSPORT PROPERTIES OF PAA MEMBRANES PREPARED FROM 10^6-MW PAA ON CN POROUS SUPPORT

Water Flux of Support at 40 psi (gfd)	Membrane Preparation			NaCl Rejection (%)	Water Flux (gfd)
	Method	Wt % PAA	Heat Treatment		
2700	Cast	4.8	None	78	1.7
				80	1.9
				75	1.3
			110°C, 1 hr	75	0.8
				81	0.9
2500			None	68	42
				68	40
				91	9.3
			80°C, 1 hr	92	7.8
			110°C, 1 hr	94	5.7
2400			None	72	59
				70	38
				68	65
				85	6.2
1800					
800				85	13
				81	13
				85	11
630					
				79	56
				72	37
				79	52
				87	17
				84	11
				95	1.0
				90	2.1
400				85	13
				82	11
				84	11
				83	12
				83	11
				84	11
				83	11
2000		4.4		83	13
				74	6
850				82	5
				72	8

TABLE 5 (Continued)

Water Flux of Support at 40 psi (gfd)	Membrane Preparation			NaCl Rejection (%)	Water Flux (gfd)
	Method	Wt % PAA	Heat Treatment		
2000	Cast	3.1	None	20	13
↓				66	4
850		↓		25	26
2000		2.6		0	113
↓				42	239
800				34	96
↓				34	99
		↓		34	99
2000		2.1	↓	76	26
750			110°C, 30 min	10	500
↓				10	530
		↓	None	20	338
				10	550
2000		1.3		28	9.5
↓				68	18
		↓		42	117
				58	69
750				36	92
↓				36	90
100	↓	↓	↓	74	4.7
800	Dip	1.0		68	13
↓		↓		62	17
				51	24
2700		0.5		33	139
290		↓		43	40
↓				40	14
1800				55	30
↓				44	54
290		0.2		45	28
1800		0.04 (2 dips)		45	69
↓		↓		38	129
				41	125
	↓	0.04 (4 dips)	↓	38	164
				39	147

membranes. Most of the membranes showed rejections of approximately 35% to 60% with fluxes of approximately 70 to 110 gfd, although several of the membranes gave fluxes of greater than 130 gfd with rejections of 40% to 50%. Higher fluxes were generally associated with the polysulfone with lower low-pressure fluxes. This relationship is believed to be due to the presence of finer pores and less intrusion of the PAA into the pores of the support. It might be expected that plugging of the pores would result from the use of very-high-flux polysulfone if large pores were present. The best membranes were prepared by casting onto polysulfone (2900 gfd) from a 4.8 wt-% PAA solution followed by heat-treating at 110° to 115°C. Membranes of this quality were not prepared from any other combination of support and casting conditions. Heat treatment above 115°C resulted in a non-flowing membrane, and it is suspected that cross-linking of the PAA occurred above this temperature.

Transport properties of 10^6-MW PAA-CN membranes are shown in Table 5. The reproducibility among these membranes is not as good as was observed for the PAA-polysulfone membranes, and there does not seem to be any correlation between low-pressure flux of the support and water flux of the membranes. No beneficial effects were observed to result from heat treatment, and fluxes were generally lower for these membranes than for the PAA-polysulfone membranes.

In Fig. 5, the data from Tables 3 and 4 are plotted and compared with cellulose 2.5-acetate membranes. Although there is only a small region of overlap, it appears that the PAA-polysulfone membranes are superior to the PAA-CN/CA membranes. Several of the high-flux PAA-polysulfone membranes exhibit flux-rejection properties comparable to those of the asymmetric cellulose 2.5-acetate membranes.

The data from Table 5 are plotted in Fig. 6. Only three of the PAA-CN membranes are comparable to the cellulose 2.5-acetate membranes. Membranes prepared from greater than 4 wt-% PAA solutions generally exhibit higher rejections and lower fluxes than membranes prepared from lower concentrations.

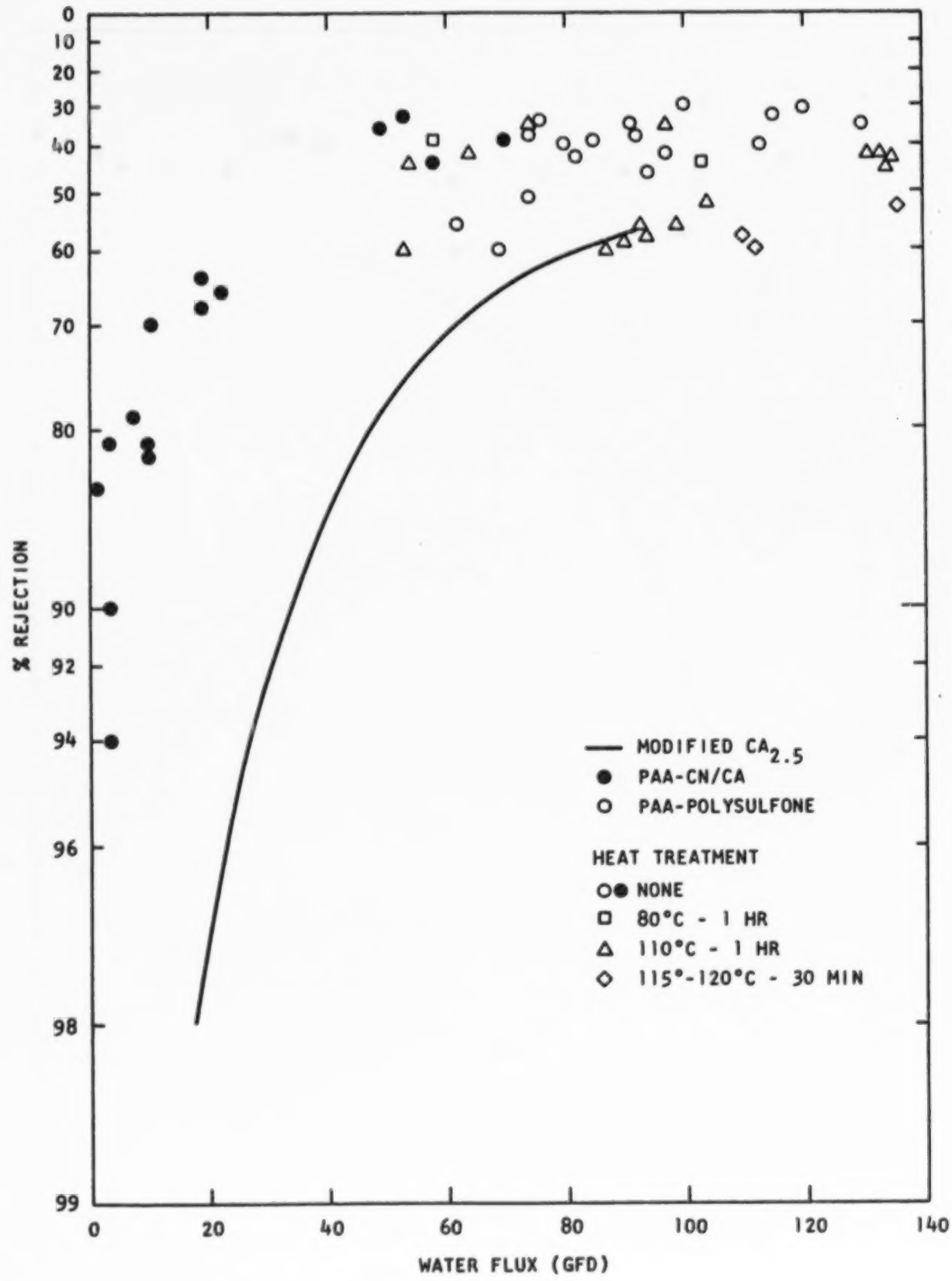

Fig. 5. Flux-rejection data for 10^6-MW PAA membranes on CN/CA and polysulfone porous supports

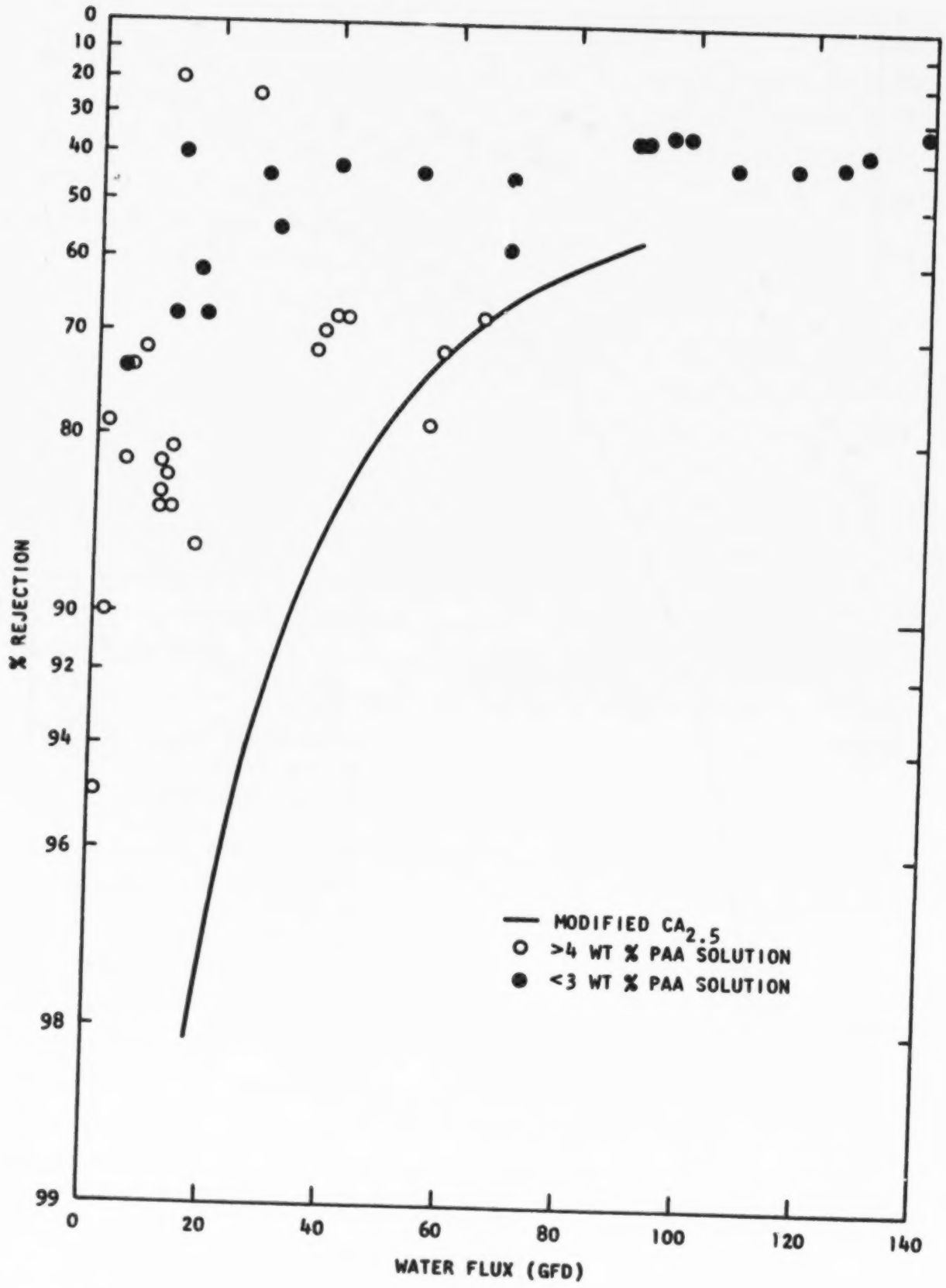

Fig. 6. Flux-rejection data for 10^6-MW PAA membranes on CN porous support

Several of the PAA-CN and PAA-polysulfone membranes were tested in long-term tests to observe changes in flux and rejection with time. In addition, these membranes were tested with Na_2SO_4, NH_4NO_3, and urea for comparison with cellulose 2.5-acetate membranes. These data are given in Tables 6 and 7 for PAA-CN and PAA-polysulfone, respectively. Three of the membranes listed in Table 6 were tested for the number of hours shown in the elapsed time column; the other membranes were installed at the indicated time. In both tables, a rapid flux decline is noted for the PAA membranes over the first two days of testing; the flux then continued to decrease at a rate of approximately 10%/day over the remainder of the test period. At the end of the tests, the water flux through the PAA membranes was generally comparable to that through the cellulose 2.5-acetate membrane. Rejections of Na_2SO_4 were all above 85%, even for membranes rejecting only approximately 36% NaCl. The rejection of NH_4NO_3 were comparable to that of NaCl, with the exception of the cellulose 2.5-acetate membranes. For these membranes, the NH_4NO_3 rejection was substantially less than for NaCl. All the membranes rejected urea poorly. This is in agreement with earlier measurements using heat-treated cellulose 2.5-acetate membranes heat-treated at 85°C; the rejection of urea was only 45% with an NaCl rejection of 98.5% (10).

An attempt was made to restore the performance of the PAA membranes by depressurizing and draining the reverse osmosis test loop and by adding 10^6-MW PAA to the feed. The results of this test are shown in Table 8. It can be seen that draining the system and flushing it with distilled water resulted in an increase in rejection and about a 10% increase in flux. No further benefit was evidenced by pressure pulsing the system. The enhancement in membrane performance was only transient; within a few hours the performance returned to the original level. (This behavior can be seen more clearly from Table 6 by noting the flux increase in membranes 120-1, -2, and -4 at 24 hr elapsed time when the system was depressurized to install membranes 120-3 and 120-5.) The addition of 10 ppm 10^6-MW PAA resulted in a sharp decrease in rejection with about a 20% increase in flux. After an additional 18 hr, the membrane properties had returned to their original level. Thus, it appears that at least partial restoration of membrane performance can be achieved by periodic depressurization.

TABLE 6
TRANSPORT PROPERTIES OF 10^6-MW PAA-CN AND CELLULOSE 2.5-ACETATE MEMBRANES

Elapsed Time (hr)	Solute	120-1[a]		120-2[a]		120-3[b]		120-4[b]		120-5[c]		CA[d]	
		Rejection (%)	Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Rejection (%)	Water Flux (gfd)
0.5	0.11% NaCl	31	140	29	137			22	332				
6		36	122	36	122			39	171				
22		36	92	36	90			43	117				
24		33	102	33	100	46	112	40	132	64	29		
27		36	98	36	96	56	89	42	125	75	28	72	70
46		36	83	36	82	58	69	45	100	76	26	72	61
47	0.09% Na_2SO_4	89	78	89	77	94.5	63	90	90	97.6	27	>99	56
51		88	77	88	74	93.7	52	89	82	96.4	25	98.9	54
52	0.09% NH_4NO_3	40	84	40	83	61	60	48	93	79	34	43	56
56		44	82	43	80	61	55	50	87	78	28	43	57
57	0.10% NaCl	37	81	37	80	63	56	47	87	83	31	71	56
119		31	60	34	59	55	42	44	60	80	20	70	51
121	0.12% urea	2	59	6	59	11	44	10	61	16	22	13	52
125		4	61	7	60	11	42	12	62	17	20	12	54
126	0.10% NaCl	39	66	39	65	63	45	49	65	84	23	71	55
143		33	59	33	57	57	42	43	58	78	19	72	52

[a] Cast from 1.3 wt % 10^6-MW PAA on CN (750 gfd at 40 psi).
[b] Cast from 1.3 wt % 10^6-MW PAA on CN (2000 gfd at 40 psi).
[c] Cast from 2.1 wt % 10^6-MW PAA on CN (2000 gfd at 40 psi).
[d] Heat-treated at 55°C for 5 min.

TABLE 7
TRANSPORT PROPERTIES OF 10^6-MW PAA-POLYSULFONE AND CELLULOSE 2.5-ACETATE MEMBRANES

Elapsed Time (hr)	Solute	126-1[a]		126-2[a]		126-3[a]		125-5[a,b]		125-6[a,b]		CA[c]	
		Rejection (%)	Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Rejection (%)	Water Flux (gfd)
0.5	0.12% NaCl	35	130	26	175	49	92	65	54	70	47		
17		43	82	38	98	60	53	63	48	70	39	71	57
25		44	76	39	90	61	50	61	52	68	42	70	55
41		47	55	42	64	60	37	59	43	66	35	68	48
42	0.09% Na_2SO_4	86	62	86	72	95.7	43	95.7	46	97.6	39	98.3	50
45		85	60	85	70	95.5	41	96.8	46	97.5	39	98.9	51
46	0.09% NH_4NO_3	55	68	51	78	64	45	64	50	69	41	41	52
50		56	65	56	74	66	42	64	48	70	41	40	52
51	0.1% NaCl	55	60	55	70	70	40	67	46	73	39	70	52
68		55	49	53	57	68	32	66	40	70	33	70	47
69	0.11% urea	5	53	5	58	5	35	7	41	8	37	10	50
73		7	50	7	57	7	31	8	39	8	32	9	51
74	0.1% NaCl	60	53	58	61	72	34	70	42	74	35	70	51
137		61	35	59	41	71	26	68	35	73	29	70	46

[a] Cast from 1.3 wt % 10^6-MW PAA + 2.1 wt % PAA on polysulfone (2500 gfd at 40 psi).

[b] Previously tested for 124 hr with 0.1% NaCl.

[c] Heat-treated in water at 55°C for 5 min.

TABLE 8
RESTORATION OF PAA MEMBRANES

Elapsed Time (hr)	10^6-MW PAA-CN								10^6-MW PAA-Polysulfone			
	NaCl Rejection (%)	Water Flux (gfd)	NaCl Rejection (%)	Water Flux (gfd)	NaCl Rejection (%)	Water Flux (gfd)	NaCl Rejection (%)	Water Flux (gfd)	NaCl Rejection (%)	Water Flux (gfd)	NaCl Rejection (%)	Water Flux (gfd)
0.5												
18									27	400	61	108
26	46	67	46	77	37	75	53	53	35	131	56	62
72	50	39	50	40	46	32	44	29	54	104	64	76
91	52	32	52	31	46	26	46	24	59	62	67	50
92.5[a]									60	53	66	41
93	62	33	62	33	57	28	51	27	67	59	74	47
95[b]												
95.5	62	33	62	33	58	28	52	27	66	59	72	47
99.5[c]												
100	47	42	47	41	44	33	41	32	49	68	56	57
117.5	53	31	54	31	52	26	48	25	63	54	69	46
118[a]												
118.5	58	33	59	33	51	27	54	27	65	54	70	47
124												

(a) Drained and flushed system; depressurized system for 5 min

(b) Depressurized system three times in rapid succession

(c) Added 10 ppm 10^6-MW PAA to system

Several sets of PAA membranes were tested in reverse osmosis at 600 psi using filtered secondary effluent from the Escondido, California, activated sludge sewage treatment plant. The effluent was filtered first through No. 40 Whatman filter paper and then through 5-μ cartridge filters installed in the test loop. Although the effluent obtained from the plant varied from day to day, a typical analysis would show approximately 1500 μmho/cm conductivity, approximately 85 mg/liter total carbon (TC), and 25 to 30 mg/liter total organic carbon (TOC). TOC analyses were performed by acidifing the sample to convert all carbonates and bicarbonates to carbon dioxide and purging the sample for 5 min with N_2 to expel the CO_2; thus, all inorganic carbon was removed. No attempt was made to determine the organic composition of the effluent. Over a period of 4 to 6 days in the test loop, both TC and TOC concentrations decreased by about 50%; little change in conductivity was noted. The decrease in TOC hampered analysis of the product water. The sensitivity of the Beckman Carbonaceous Analyzer was about 1 mg carbon/liter, and many of the product water samples were below this limit.

Flux and rejection data for tests performed with secondary effluent are presented in Tables 9 through 13. These tables also contain flux and rejection data for 0.1% NaCl taken immediately before draining and flushing the system prior to adding the secondary effluent. Tables 12 and 13 additionally show data for NaCl taken 30 min and 24 hr after the end of the effluent test. The system was drained, then flushed with water for 20 min, and 0.1% NaCl solution was added.

Tables 9 and 10 show the rejection of secondary effluent by 300,000-MW PAA-CN/CA membranes. The membranes listed in Table 9 show about a 20% increase in flux after addition of the effluent (as a result of flushing the system), followed by a substantial decrease over the next 24 hr. No further decrease in flux is noted over the next 4 days. The data in Table 10 show an immediate flux decline of about 30% with essentially no change for the next 2-1/2 days. It is noted that the cellulose 2.5-acetate membrane displayed no significant change in flux or rejection during the test. This indicates that the flux decline is a result of fouling of the PAA membranes, not a compaction phenomenon as is frequently observed (4). In both tests the

TABLE 9
REJECTION OF FILTERED SECONDARY EFFLUENT
BY 300,000-MW PAA-CN/CA MEMBRANES

Elapsed Time (hr)	Membrane	0.1% NaCl		Secondary Effluent			
					Rejection (%)		
		Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Conductivity	Total Carbon	Total Organic Carbon
---	66-1	22	81				
	-2	20	76				
	-3	23	80				
0.5	66-1			25	74	72	83
	-2			26	67	66	87
	-3			27	72	72	94.1
6	66-1			26	71	74	84
	-2			27	67	66	90
	-3			27	71	73	94.1
23	66-1			15	74	68	76
	-2			14	70	70	88
	-3			15	73	65	94.1
50	66-1			14	72	74	96.0
	-2			13	70	72	>96.8[a]
	-3			14	70	73	>96.8[a]
120	66-1			16	71		
	-2			15	70		
	-3			16	71		

[a]Limit of sensitivity

TABLE 10
REJECTION OF FILTERED SECONDARY EFFLUENT BY 300,000-MW PAA-CN/CA AND CELLULOSE 2.5-ACETATE MEMBRANES

Elapsed Time (hr)	Membrane	0.1% NaCl		Secondary Effluent			
					Rejection (%)		
		Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Conductivity	Total Carbon	Total Organic Carbon
---	70-1[a]	19	73				
	-2[a]	14	85				
	-3	18	84				
	CA[b]	38	89				
1	70-1			13	75	74	84
	-2			9.7	84	80	84
	-3			12	83	82	95.5
	CA			38	93.7	97.5	>96.8[c]
17	70-1			11	72	72	88
	-2			8.1	87	84	82
	-3			9.7	84	83	93.0
	CA			33	94.3	96.8	>96.8[c]
52	70-1			13	61	73	76
	-2			8.7	84	88	88
	-3			9.7	82	92.7	>96.8[c]
	CA			34	92.9	97.5	>96.8[c]
66	70-1			15	50	56	67
	-2			8.1	85	86	85
	-3			9.2	83	92.5	>96.8[c]
	CA			38	92.8	97.5	>96.8[c]

[a] Heat-treated in air at 80°C for 1 hr.

[b] Heat-treated in water at 70°C for 5 min.

[c] Limit of sensitivity

TABLE 11
REJECTION OF SECONDARY EFFLUENT BY 10^6-MW PAA-CN AND CELLULOSE 2.5-ACETATE MEMBRANES

Elapsed Time (hr)	Membrane	0.1% NaCl		Secondary Effluent[a]			
					Rejection (%)		
		Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Conductivity	Total Carbon	Total Organic Carbon
---	101-1	56	74				
	-2	54	76				
	-3	56	74				
	-4	62	62				
	-5	70	58				
	CA[b]	45	73				
1	101-1			18	58	75	91.3
	-2			17	64	78	>95.6[c]
	-3			17	59	74	>95.6[c]
	-4			17	48	66	83
	-5			19	45	64	83
	CA			29	85	96.5	>95.6[c]
18	101-1			1.8	75	86	>95.6[c]
	-2			1.7	79	88	>95.6[c]
	-3			1.7	78	83	>95.6[c]
	-4			1.7	69	82	>95.6[c]
	-5			1.8	64	79	>95.6[c]
	CA			1.4	74	90	>95.6[c]

(a) Effluent was prefiltered only through No. 40 Whatman filter paper.
(b) Heat-treated in water at 60°C for 5 min.
(c) Limit of sensitivity

TABLE 12
REJECTION OF FILTERED SECONDARY EFFLUENT
BY 10^6-MW PAA-CN AND CELLULOSE 2.5-ACETATE MEMBRANES

Elapsed Time (hr)	Membrane	0.1% NaCl		Secondary Effluent			
					Rejection (%)		
		Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Conductivity	Total Carbon	Total Organic Carbon
---	120-1	59	33				
	-2	57	33				
	-3	57	42				
	-4	58	43				
	-5	19	78				
	CA[a]	52	72				
0.5	120-1			48	22	39	55
	-2			48	22	39	52
	-3			30	38	54	63
	-4			47	30	48	61
	-5			12	60	74	78
	CA			48	77	85	72
3	120-1			35	30		
	-2			35	30		
	-3			22	46		
	-4			32	36		
	-5			9.3	67		
	CA			35	79		
19	120-1			18	38	56	63
	-2			18	38	56	63
	-3			13	54	65	71
	-4			16	44	61	69
	-5			7.2	72	75	75
	CA			18	80	85	75
43	120-1			16	38	58	71
	-2			16	38	58	63
	-3			12	54	65	71
	-4			15	47	63	71
	-5			7.2	74	75	83
	CA			15	81	85	75

TABLE 12 (Continued)

Elapsed Time (hr)	Membrane	0.1% NaCl		Secondary Effluent			
					Rejection (%)		
		Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Conductivity	Total Carbon	Total Organic Carbon
45(b)	120-1			16	38		
	-2			16	38		
	-3			12	54		
	-4			15	47		
	-5			7.2	74		
	CA			15	81		
67	120-1			17	38	56	70
	-2			17	38	56	70
	-3			13	55	67	79
	-4			15	47	62	75
	-5			7.8	73	78	79
	CA			14	81	81	83
139	120-1			18	35	56	67
	-2			18	35	56	67
	-3			14	54	66	67
	-4			17	43	61	72
	-5			8.6	70	72	>90(c)
	CA			14	78	89	>90(c)
140	120-1	33	45				
	-2	33	45				
	-3	29	67				
	-4	37	54				
	-5	14	84				
	CA	47	65				
162	120-1	33	39				
	-2	33	39				
	-3	29	60				
	-4	36	48				
	-5	15	79				
	CA	47	69				

(a) Heat-treated in water at 55°C for 1 hr

(b) System was depressurized rapidly at 44.5 hr elapsed time.

(c) Limit of sensitivity

TABLE 13
REJECTION OF FILTERED SECONDARY EFFLUENT
BY 10^6-MW PAA-POLYSULFONE AND CELLULOSE 2.5-ACETATE MEMBRANES

Elapsed Time (hr)	Membrane	0.1% NaCl		Secondary Effluent			
					Rejection (%)		
		Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Conductivity	Total Carbon	Total Organic Carbon
	126-1	35	61				
	-2	41	59				
	-3	26	71				
	-5	35	68				
	-6	29	73				
	CA[a]	46	70				
0.5	126-1			27	52	64	78
	-2			28	49	65	73
	-3			28	57	66	73
	-5			37	53	68	89
	-6			34	65	74	89
	CA			46	81	90	89
3	126-1			24	54		
	-2			24	50		
	-3			27	59		
	-5			36	59		
	-6			36	64		
	CA			44	82		
19	126-1			16	57	68	>94[b]
	-2			16	52	67	88
	-3			18	60	71	93.9
	-5			29	60	75	93.9
	-6			30	66	77	>94[b]
	CA			33	82	91.9	>94[b]

TABLE 13 (Continued)

Elapsed Time (hr)	Membrane	0.1% NaCl		Secondary Effluent			
					Rejection (%)		
		Water Flux (gfd)	Rejection (%)	Water Flux (gfd)	Conductivity	Total Carbon	Total Organic Carbon
43	126-1			13	56	69	>94[b]
	-2			13	53	66	93.9
	-3			15	59	70	88
	-5			26	61	70	88
	-6			27	66	72	70
	CA			27	82	88	88
67	126-1			12	54	57	76
	-2			12	51	58	79
	-3			14	57	60	76
	-5			24	60	64	70
	-6			26	64	67	70
	CA			24	81	82	88
68	126-1	23	74				
	-2	23	71				
	-3	30	74				
	-5	52	77				
	-6	54	80				
	CA	43	68				
92	126-1	25	67				
	-2	25	64				
	-3	28	66				
	-5	46	69				
	-6	47	74				
	CA	42	67				

(a) Heat-treated in water at 55°C for 5 min.

(b) Limit of sensitivity

conductivity rejections were about the same as the TC rejections, with TOC rejections being slightly higher.

Table 11 gives the results of a test using 10^6-MW PAA-CN membranes. In this test the effluent was prefiltered only through No. 40 Whatman paper and the 5-μ filter cartridges were eliminated. Immediate and severe flux decline was observed for all membranes (while rejection improved for all but the CA membrane), and the decline continued until 18 hr, when the test was terminated. This behavior illustrates the necessity for prefiltering the effluent through a good filter system to prevent membrane fouling. These membranes showed significantly higher TC rejection than conductivity rejection and almost complete TOC rejection.

Tables 12 and 13 show flux and rejection data for 10^6-MW PAA-CN and PAA-polysulfone membranes, respectively. The membranes used in these tests were initially tested for up to 143 hr with NaCl, Na_2SO_4, NH_4NO_3, and urea (see Tables 6 and 7). An appreciable initial flux decline was observed with the PAA-CN membranes (Table 12) that was not as pronounced with the lower-flux PAA-polysulfone membranes (Table 13). This decline was not observed with the cellulose 2.5-acetate control membranes. All membranes showed flux decline for the first 2 days; the flux then remained relatively constant for the duration of the test. Both sets of membranes gave higher TC rejections than conductivity rejections, with somewhat higher TOC rejections. It is noted that all rejections become somewhat poorer with the PAA-polysulfone and cellulose 2.5-acetate membranes after 43 hr. It is suspected that these data are the result of a slight loss of sensitivity of the carbonaceous analyzer, since no evidence of membrane deterioration was seen in the longer test with PAA-CN membranes. Removal of the effluent from the system, flushing, and the addition of 0.1% NaCl resulted in a flux increase of about a factor of 2 for the PAA membranes and a factor of 2 to 3 for the cellulose 2.5-acetate membranes. After an additional day, a slight decrease in rejection was noted, with no substantial changes in flux.

Membranes were also cast from five polyelectrolytes, other than PAA, and evaluated in reverse osmosis tests. The transport properties of these membranes are given in Table 14. The various concentrations of polyelectrolytes were chosen to provide a solution viscous enough for casting. With the possible exception of Polyhall 295, a high-molecular-weight anionic polyacrylamide, none of these polyelectrolytes showed any superiority over PAA with respect to flux and rejection properties.

In summary, although a few PAA membranes were prepared with transport properties comparable to those of asymmetric cellulose 2.5-acetate membranes, the lack of reproducibility and severe flux decline shown by these membranes may make them unsuitable for use in waste-water reclamation. While PAA is not subject to hydrolysis and may therefore prove to have some lifetime advantages over cellulose acetate, unless a method is found to improve the rejection without affecting the flux, the asymmetric cellulose acetate membrane will remain preferable because of its greater rejection capability.

PVP-POLYISOCYANATE INTERPOLYMERS

HOMOGENEOUS FILMS

Extensive characterization studies were carried out on two different PVP films. One had a PMPI:PVP molar ratio of 0.7 and the other had a ratio of 0.9. Both of these films (designated PVP 0.7 and PVP 0.9) were prepared from the blocked PMPI.

The permeabilities to each of the solutes studied in direct osmosis and reverse osmosis tests are given in Table 15, and similar data for homogeneous cellulose 2.5-acetate membranes are included for comparison. The tabulated distribution coefficient values were obtained from desorption rate experiments. Solute concentrations used in direct osmosis and desorption rate tests were 10% for arabinose and dextrose, and 1% for all other solutes. All the solute concentrations in reverse osmosis tests were approximately 0.1%, with the exception of the NaCl concentration, which was 0.9%. The predicted rejection for each solute in reverse osmosis at 1500 psi was calculated from

TABLE 14
TRANSPORT PROPERTIES OF POLYELECTROLYTE MEMBRANES
CAST ON CN POROUS SUPPORT (850 GFD AT 40 PSI)

Polyelectrolyte	Percent Solids	Water Flux (gfd)	NaCl Rejection (%)
Cyanamer A-370	2.5	28	24
		17	24
Cyanamer P-26	2.5	18	19
		31	19
Polyhall 402	1.0	92	18
		85	18
Polyhall 295	1.25	62	41
		68	39
Polyvinylmethylether-maleic acid (PVME-MA)	5.0	61	13
		66	13

TABLE 15
PERMEABILITY OF PVP-PMPI AND CELLULOSE 2.5-ACETATE MEMBRANES TO WATER AND VARIOUS SOLUTES

Solute	Desorption Rate, K $\left(\frac{g/cm^3}{g/cm^3}\right)$	Direct Osmosis			Reverse Osmosis (1500 psi)	
		$D_1c_1 \times 10^6$ (g/cm-sec)	$D_2K \times 10^8$ (cm^2/sec)	Calculated Rejection (%)	$D_1c_1 \times 10^6$ (g/cm-sec)	Measured Rejection (%)
PVP 0.7						
NaCl	0.16	2.9	9.5	70	1.9	55
Dextrose	0.26		3.0	88		
Arabinose	0.17		3.9	85	2.0	80
Glycine			5.6	79	2.6, 1.5	76, 82
Acetic acid	1.0		3.0	20	2.1	12
NH_4Cl		2.9	25	45	1.8	5.7
$NaNO_3$			21	50	1.8	56
PVP 0.9						
NaCl	0.16	0.73	0.78	88	0.64, 0.57	84, 84
Arabinose	0.17		0.15	97	0.71	92
Glycine	0.15		0.17	96	0.62, 0.49	92, 93
Acetic acid	1.3		9.0	20	0.69, 0.63	14, 15
NH_4Cl		0.73	1.4	80	0.65, 0.58	86, 85
$NaNO_3$			1.0	84	0.66, 0.59	86, 86
NH_4NO_3			2.6	67	0.74, 0.66	68, 67
Cellulose 2.5-Acetate						
NaCl	0.035[a]	0.26[a]	0.016	99.5	0.23	99.2
Arabinose					0.23	94
Glycine					0.20	95
Acetic acid					0.26	-13
NH_4Cl					0.24	98
$NaNO_3$					0.24	96
NH_4NO_3					0.25	95

[a] Reference 8

the permeabilities observed in direct osmosis. Good agreement was obtained for almost all solutes. The only major discrepancy was observed with acetic acid, where the measured rejection was only 12% for PVP 0.7 and 14% for PVP 0.9. These values were lower than the predicted rejections.

For each of the solutes except acetic acid, the permeability decreased at least a factor of 10 with increased polyisocyanate content. This was apparently the result of the less hydrophilic nature of the membranes and the decreased mobility of the PVP chains. For the three solutes checked, the distribution coefficient was essentially unchanged. The distribution coefficient was much higher for acetic acid than for the other solutes, and it increased with increasing isocyanate content. The distribution coefficient for most of the solutes was much less than unity.

The good agreement between the predicted and measured values of rejection for most solutes indicates that coupling of water and solute flow does not occur in these cases and that the homogeneous films were imperfection-free (19). Because water and solute flows in direct osmosis are in opposite directions, whereas in reverse osmosis they are in the same direction, there should have been a noticeable difference in the apparent solute permeability if flow coupling occurred or if imperfections were present. The difference between the calculated and measured values of rejection for acetic acid, however, suggests that acetic acid transport does not occur only by a solution-diffusion mechanism but rather was coupled to the water flow. The small enrichment (negative rejection) of acetic acid observed with the cellulose 2.5-acetate membrane was also probably the result of flow coupling, although no coupling coefficients were determined in this study.

For the organic materials, glycine and arabinose, the rejection by the PVP 0.9 membrane and the cellulose 2.5-acetate membrane was about the same. The water permeability of the PVP 0.9 is about three times higher than that of the cellulose 2.5-acetate.

ASYMMETRIC MEMBRANES

Reverse osmosis results for membranes prepared from unblocked PMPI are shown in Table 16. These membranes were prepared from a stock solution (10 wt-% solids) having a 1:1 ratio of moles PVP:equivalents PMPI (0.84 g PVP/g PMPI) and air-dried for 24 hr. Two of the membranes were cast from solutions containing 30% THF. These tests were conducted at 1500 psi and 25°C using 1% NaCl as feed.

Clearly, the addition of THF increased the water flux substantially (five- to ten-fold), and the fact that good salt rejection was maintained indicates that the higher flows did not result from imperfections. The membranes appeared to be skinned on the air-dried surface. The thickness of the skin can be estimated if two assumptions are made. The first assumption is that the flow resistance is all in the skin and that the flux is inversely proportional to the skin thickness. The fact that the thickest membrane exhibited the highest flow indicates that gross thickness per se is not important. The second assumption is that the flow of water can be divided into two parts: a diffusive flux of essentially pure water, and a leak through flaws in the structure which permits the flow of undiluted brine. The percent solute rejection is nearly the same as the percent of the total flow which is diffusive, and it is the diffusive flow which must be used to estimate the thickness of the skin.

For the third membrane listed in Table 16, the diffusive flow of water is 0.58 x 0.96 = 0.56 gfd. The thickness of the thin skin can then be calculated to be (0.096/0.56) x 25 = 4.3 μ. The calculated thickness of the last membrane in the table is 2.4 μ. These membranes were made under nominally the same conditions, and this difference is random scatter. While these calculations should not be considered quantitative, they do illustrate the fact that THF addition produced asymmetric membranes with skin thicknesses only a few percent of the gross thickness.

Since the solution containing THF tended to react in the mixing flask before casting due to the presence of traces of water, the effect of time after solution preparation (solution age) was investigated. The level of solids content and the percent THF in the solution were also determined. The effects of these variables are shown in Table 17. In each case, the air-drying time was 18 hr. The data are sufficiently scattered that no important effect of solution age or composition is apparent. The skin thicknesses, estimated using the technique described above, ranged from 3% to 30% of the total membrane thickness.

The water fluxes in Table 17 are lower than desired, presumably because on drying the dense skin became too thick. Since it was believed, based on other studies (22), that pyridine accelerated the isocyanate-water reaction, small quantities of pyridine were added to a 10 wt-% PVP-PMPI solution in chloroform in an attempt to produce a coherent film in a much shorter drying time. The THF was completely replaced with pyridine in another variation in the solution, again to reduce the required drying time. The data obtained with these membranes are given in Table 18.

With a trace of pyridine, coherent films with properties comparable to those obtained with overnight drying were produced with only several minutes air-dry time. In the absence of THF, coherent films were produced with short air-dry time, but the rejections were all significantly lower. In no case was high rejection combined with high water flux.

Aqueous annealing did not appear to improve membrane performance. Some of the membranes described in Table 18 were heated for several hours in water at 95°C. The flux and rejection data obtained with 0.1% NaCl feed are shown in Table 19. Again, the data are widely scattered and none of the membranes combined high flux with high salt rejection.

Two other additives were tested at several concentrations and drying times with the 10 wt-% PVP-PMPI stock solution. Triethyl phosphate (TEP) was used in concentrations from 5% to 20%, and the membranes were tested both as-cast and after heating in water. The drying times chosen were the

TABLE 16
EFFECT OF THF ON PROPERTIES OF PVP-PMPI MEMBRANES

Casting Solvent	Thickness (μ)	Water Flux (gfd)	Rejection (%)
$CHCl_3$	25	0.096	99
$CHCl_3$	25	0.096	99
$CHCl_3$-30% THF	34	0.58	96
$CHCl_3$-30% THF	73	1.09	93

TABLE 17
EFFECT OF SOLUTION AGE AND COMPOSITION ON THE PROPERTIES OF PVP-PMPI MEMBRANES

Solids in Stock Solution (wt %)	Percent THF Additive	Solution Age (hr)	Water Flux (gfd)	NaCl Rejection (%)	Membrane Thickness (μ)	Calculated Skin Thickness (μ)
15	40	1/4	0.43	90	66	6.1
15	40	1	0.22	98	73	11
15	40	6-1/2	0.37	95	76	6.8
10	30	5	1.1	87	38	2.5
10	30	5	1.9	78	49	1.6
10	30	9-3/4	0.26	80	36	11
10	30	9-3/4	0.83	72	76	4.0
10	30	21	0.43	90	61	6.2
10	30	21	0.52	88	82	5.2

TABLE 18
EFFECT OF PYRIDINE ON PVP-PMPI MEMBRANE PROPERTIES

Additive	Percent Additive	Drying Time (min)	Membrane Thickness (μ)	Water Flux (gfd)	NaCl Rejection (%)
THF+1% pyridine	30	5	(a)	(a)	(a)
THF+1% pyridine	30	20	32	0.12	96
THF+1% pyridine	30	20	71	0.32	96
Pyridine	30	10	61	18	10
Pyridine	30	10	50	19	10
Pyridine	30	15	36	1.9	40
Pyridine	30	15	34	1.3	50
Pyridine	30	7	77	8.7	10
Pyridine	30	7	66	9.4	10
Pyridine	20	7.5	89	24.0	4
Pyridine	20	7.5	93	4.3	12
Pyridine	20	10	71	1.4	43
Pyridine	20	10	84	1.9	29

(a) Membrane was too weak to test.

TABLE 19
EFFECT OF HEATING ON PVP-PMPI MEMBRANE PROPERTIES

Percent Pyridine	Drying Time (min)	Heating Time (hr)	Water Flux (gfd)	NaCl Rejection (%)
20	7.5	2	2.9	21
20	7.5	5	3.1	14
20	10	2	0.8	61
20	10	5	1.0	61
30	7	2	13	6
30	7	5	12	8

minimum times required to obtain a coherent film. The data are summarized in Table 20. Increased TEP content increased the water flux but decreased the salt rejection. Heating did not improve the rejection, nor did it appear to reduce water flux; however, the fluxes were all too low to be of interest.

Amyl acetate, which is quite compatible with the chloroform-PVP-PMPI system, was also tried as an additive at 10% concentration to the 10 wt-% PVP-PMPI stock solution. The results are given in Table 21. The very low fluxes and poor rejections indicate that a porous structure did not form as the chloroform evaporated.

When the difunctional isocyanate, MDI, was substituted in order to produce a linear, rather than a three-dimensional, polymer, the membrane had essentially the same properties as membranes made from PMPI and was not responsive to heat-treating.

In summary, with none of the techniques studied was it possible to make an asymmetric membrane from a PVP-polyisocyanate based system with the same rejection properties as the homogeneous membrane.

CELLULOSE DIACETATE

The permeability of a single homogeneous cellulose diacetate membrane to water and several solutes was measured in direct osmosis experiments. The permeability data were used with Eq. 13 to calculate a predicted solute rejection under reverse osmosis operating conditions of 100-atm net pressure. The measured permeabilities and calculated solute rejections are given in Table 22. The water permeability (D_1c_1 = 1.2 x 10^{-6} g/cm-sec) was measured only with NaCl and was assumed to be similar for the other solutes. The value for NaCl is in substantial agreement with that previously obtained by Lonsdale, Merten. and Riley (8).

The investigation of cellulose diacetate was terminated because of the low rejection calculated for the organic materials.

TABLE 20
EFFECT OF TEP ON PVP-PMPI MEMBRANE PROPERTIES

Percent TEP	Drying Time (min)	Heating Time at 95°C (hr)	Membrane Thickness (μ)	Water Flux (gfd)	NaCl Rejection (%)
5	15	0	84	0.4	75
5	15	0	89	0.7	64
10	10	0	109	5.2	24
10	10	0	133	4.7	24
20	10	0	140	10	17
20	10	0	155	6.9	17
10	10	2	110	3.7	22
10	10	5	131	5.2	11
20	10	2	171	11	15
20	10	5	126	12	7.5

TABLE 21
EFFECT OF AMYL ACETATE ON PVP-PMPI MEMBRANE PROPERTIES

Air-Dry Time (min)	Membrane Thickness (μ)	Water Flux (gfd)	NaCl Rejection (%)
10	104	0.26	20
10	110	0.19	38
10	110	0.15	26
17	90	0.52	10
17	90	0.17	4

TABLE 22
TRANSPORT PROPERTIES OF CELLULOSE DIACETATE

Solute Composition	D_2K (cm^2/sec)	Calculated Rejection at 100 atm (%)
1% NaCl	1.9×10^{-8}	81
1% $NaNO_3$	3.7×10^{-8}	70
1% NH_4Cl	1.5×10^{-8}	85
10% arabinose	2.4×10^{-8}	79
1% acetic acid	1×10^{-7}	47

LATEX MEMBRANES

A number of reverse osmosis measurements were made on membranes cast from latices on porous CN/CA supports. The method of applying the latex, the solids content of the latex solution, and postcasting treatments such as heating in air were examined. The original observation (9) of very high water fluxes (greater than 100 gfd) with moderate salt rejection was not made for any of these variations. In only one case, in fact, was any salt rejection observed. In that instance, General Latex RA-150-7 was dissolved in dimethylformamide (1 ml of latex in 19 ml DMF). This solution was then used to prepare films approximately 4 μ thick supported on CN/CA porous supports. When tested in reverse osmosis at 800 psi, they provided 25% to 30% NaCl rejection at low water fluxes (0.1 gfd). It seems likely that the rejection observed earlier (9) with the latices was the result of formation of a dynamic membrane from some contaminant in the test loop that was not present when these experiments were performed.

SECTION 5

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SECTION 6

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27 Abstract

An experimental program was carried out to evaluate potential reverse osmosis membranes for the tertiary treatment of secondary sewage effluent. The evaluation program consisted of both direct osmosis and reverse osmosis tests on various membranes using both single solutes and secondary effluent. The types of membranes tested were polyurethane latices, cellulose diacetate, cellulose 2.5-acetate, polyvinylpyrrolidone (PVP)-polyisocyanate interpolymers, and polyelectrolytes.

The cellulose diacetate, polyurethane latices, and PVP membranes were not suitable for waste-water treatment. Although rejection of most solutes by PVP membranes was quite good for dense, homogeneous membranes, high-flux, asymmetric membranes had poor rejection characteristics. Very-high-flux membranes were prepared from polyacrylic acid cast onto cellulose nitrate, cellulose nitrate-cellulose acetate, and polysulfone porous supports. While NaCl rejection of over 80% was obtained at fluxes of less than 20 gal/ft^2-day at 600 psi, increased flux was obtained only at the expense of good rejection. The best combination of high flux and rejection was obtained with asymmetric cellulose 2.5-acetate membranes heat-treated in water at 55° to 70°C.

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